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**CLAIMS**

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[Claim(s)]

[Claim 1] Respectively a metal ball lightning pole and a metal plate electrode counter, and are arranged, and a plate electrode is made into the configuration which is in agreement with a desired surface treatment pattern. The diameter of a ball lightning pole is made smaller than a plate electrode, and a substrate is installed in inter-electrode [ with which the field which counters other electrodes of one / at least / electrode is completely covered with the solid dielectric ]. Under the pressure near the atmospheric pressure of the mixed gas of reactant gas and inert gas The surface treatment approach of the substrate characterized by impressing an electrical potential difference to an electrode, generating the discharge plasma, contacting the active species by which it was excited in the plasma on a substrate front face, and carrying out surface treatment of the substrate by the same pattern as a plate electrode configuration.

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Industrial Application] About the surface treatment approach of substrates, such as plastics, paper, a metal, glass, and ceramics, in more detail, this invention carries out surface treatment of some substrates by the plasma partially, and relates to the approach for performing plasma surface treatment in the shape of [ desired ] a pattern.

[0002]

[Description of the Prior Art] Before, the surface treatment approach by the low-pressure glow discharge plasma of 0.1 - 10Torr extent is widely learned as the approach of wettability control of the front face of substrates, such as plastics, paper, a metal, glass, and ceramics, or surface qualification, and, also industrially, it is applied. In this surface treatment approach, if it becomes a high pressure from the above-mentioned pressure, since discharge becomes local, it will shift to arc discharge and use to heat-resistant scarce plastics or a substrate like paper will become difficult, the above-mentioned pressure range is usually chosen so that it can apply to all substrates. For this reason, on the need of making it a vacuum (or low voltage), the container for processing needs an expensive vacuum chamber, and evacuation equipment is needed. Furthermore, if it is going to process to the substrate of a large area in order to process in a vacuum, a mass vacuum housing is needed and a high power thing is required also for evacuation equipment. Therefore, there was a trouble that facility costs became high. Moreover, when surface treatment of a substrate with high water absorption was performed, long duration was taken to make it a vacuum and there was also a trouble that a processing article became cost quantity.

[0003] Then, in order to conquer the above-mentioned various troubles, low-cost-izing of equipment and a facility and the discharge plasma treatment under the atmospheric pressure in which the processing to a large area substrate is possible have been proposed. For example, the surface treatment approach of performing the discharge plasma to JP,2-15171,A under atmospheric pressure by the approach of using a thin line mold electrode for JP,2-48626,B by the approach of arranging a solid dielectric in an electrode surface is proposed. By these proposals, the approach of supplying and carrying out plasma treatment of the mixed gas of the inert gas and reactant gas which are mainly concerned with helium near the substrate from the perforated pipe which has two or more puncturing is used.

[0004] With the discharge plasma treatment technique in these conventional low voltage and atmospheric pressure, when carrying out surface treatment of some substrates partially and performing surface treatment in the shape of a pattern, the photopolymer of a publication etc. is applied to JP,1-124847,A, the mask of the unnecessary part is carried out, and the method of removing the mask after plasma treatment is proposed (Tsugio Yamaoka, the Morita \*\*\*\*, a photopolymer, and KYORITSU SHUPPAN Co., Ltd. (1988)). However, there was a trouble that a process became complicated, by this approach.

[0005]

[Problem(s) to be Solved by the Invention] The purpose of this invention is to carry out surface treatment of some substrates by the plasma partially, and offer the simple approach for performing plasma surface treatment in the shape of [ desired ] a pattern.

[0006]

[Means for Solving the Problem] A metal ball lightning pole and a metal plate electrode counter, and the surface treatment approach of the substrate of this invention is arranged, respectively. A plate electrode is made into the configuration which is in agreement with a desired surface treatment pattern, and the diameter of a ball lightning pole is made smaller than a plate electrode. A substrate is installed in inter-electrode [ with which the field which counters other electrodes of one / at least / electrode is completely covered with

the solid dielectric ]. Under the pressure near the atmospheric pressure of the mixed gas of reactant gas and inert gas An electrical potential difference is impressed to an electrode, the discharge plasma is generated, the active species by which it was excited in the plasma is contacted on a substrate front face, and it is characterized by carrying out surface treatment of the substrate by the same pattern as a plate electrode configuration.

[0007] In this invention, mainly by forming formation of a surface functional group layer, formation of a free radical layer, a hydrophilic property, and a water-repellent thin film etc., the surface preparation of a substrate controls the surface energy of a substrate, makes the thin film of minerals or the quality of organic form in reforming the wettability and the adhesive property of a substrate, and a substrate front face, and points out chemical, mechanical, optical, and giving electrical characteristics etc. to a substrate.

[0008] As reactant gas used by this invention, it activates in the discharge plasma, it is contacted with a substrate, and the gas which gives water repellence to a substrate or gives a hydrophilic property to it is mentioned. For example, when giving water repellence to a substrate, the gas of fluorine content is used. As gas of fluorine content, the compound with which some fluorines of fluoride sulfur compound [, such as halocarbon gas; 6 sulfur fluorides (SF<sub>6</sub>), such as carbon fluoride gas; 1 chlorination 3 carbon etc. fluoride (CClF<sub>3</sub>), such as 6 6 fluoride / 4 fluoride / carbon / (CF<sub>4</sub>) and carbon / (CF<sub>3</sub>CF<sub>3</sub>), propylene, etc. fluoride (CF<sub>3</sub> CFCF<sub>3</sub>), ]; and these compounds were permuted by hydrogen is mentioned. It is safe and 6 4 fluoride [ carbon ], carbon, etc. fluoride etc. which do not generate toxic gases, such as hydrogen fluoride, are [ among these ] desirable.

[0009] Moreover, when giving a hydrophilic property, in order to make the layer which has functional groups, such as a carbonyl group, hydroxyl, and an amino group, form in a front face, the gas of a hydrocarbon compound is used. As the above-mentioned hydrocarbon compound, for example Methane, ethane, a propane, Alkanes, such as butane, a pentane, and a hexane; Ethylene, a propylene, Alkadiene, such as alkenes; pentadienes, such as a butene and a pentene, and a butadiene; Acetylene, Alkynes, such as methylacetylene; Benzene, toluene, a xylene, Aromatic hydrocarbon, such as an indene, naphthalene, and a phenanthrene; A cyclopropane, Cycloalkanes, such as a cyclohexane; Cycloalkene; methanols, such as cyclopentene and a cyclohexene, Alcohols, such as ethanol; aldehydes, such as ketones; methanals, such as an acetone and a methyl ethyl ketone, and ethanal, are mentioned, and these may be used independently and may be used together two or more sorts. Moreover, it is also possible to use the mixed-gas; steam; ammonia gas; nitrogen gas of oxygen gas; oxygen and hydrogen etc. in this case. Moreover, although the gas of fluorine content may be added 50% or less in these gas, water repellence will be shown if it adds exceeding this amount. In order for homogeneity to improve surface treatment, as for the above-mentioned reactant gas, it is desirable that it is in a gas condition under the pressure near the atmospheric pressure.

[0010] in order [ moreover, / chemical to a substrate mechanical, optical, and in order to give electrical characteristics etc. ] -- SiO<sub>2</sub>, TiO<sub>2</sub>, and SnO<sub>2</sub> etc. -- when forming a metallic-oxide thin film, the gas or the steams of an organic metal compound, such as hydrogenation metal gas, halogenation metal gas, or a metal alcoholate, are used.

[0011] As inert gas used by this invention, although the simple substance or mixed gas of rare gas, such as helium, Ne, Ar, and Xe, is used, it is desirable to use helium advantageous to the life of a metastable excitation state understanding reactant gas an excited part for a long time. To use inert gas other than helium, it is necessary to mix hydrocarbon gas, such as organic substance steams, such as an acetone within 2 volume %, and a methanol, and methane, ethane.

[0012] When giving water repellence to a substrate, although it is not exceptionally restrictive, since the discharge plasma does not occur even if it will impress the high voltage, if the gas of fluorine content becomes more than 10 volume %, under 10 volume % of the mixing ratio of the gas of fluorine content and inert gas is desirable, and 0.3 - 5.0 volume % in which the water-repellent grant with little amount of the gas used of fluorine content is possible is desirable [ a mixing ratio ].

[0013] It is not limited, but plastics, a metal, glass, a ceramic, paper, fiber, etc. are mentioned, and the quality of the material, especially a configuration, etc. do not care about with the quality of nonporous, or porosity the substrate used for this invention. As plastics, a film or sheets, such as polyethylene terephthalate and polyethylenenaphthalate, can be used, for example. [, such as polyester; polyethylene or polypropylene, ] [, such as a polyolefine; polystyrene; polyamide; polyvinyl chloride; polycarbonate; polyacrylonitrile, ] In the case of a film, what was extended may also be a non-extended thing. Moreover, what performed well-known processing of surface washing or surface-activity-izing may be used.

[0014] Based on drawing, this invention is explained to an example for the case where water repellence is given to below on the surface of a plastic plate at a detail. Drawing 1 is the typical sectional view showing

an example of the plasma generator used for this invention. This equipment consists of the power supply section 1, a processing container 2, a ball lightning pole 3 of the globular form arranged face to face, and a plate-like plate electrode 4.

[0015] Impression of the electrical potential difference of the frequency of the base of 5-100kHz of a power supply section 1 is enabled, and its frequency of 10-30kHz with little effect in a substrate is desirable to processing of a heat-resistant low substrate. It is desirable to impress an electrical potential difference so that it may become field strength 5 - 40 kV/cm extent, since the behavior which will shift to arc discharge if it takes [ although it carries out when discharge plasma formation impresses an electrical potential difference to an electrode, if applied voltage becomes low, since a plasma consistency and self-bias will become small / processing ] time amount and is inefficient and becomes high is shown.

[0016] Top-face 2a and base 2b is [ product made from stainless steel and side-face 2c ] the products made from Pyrex glass, and, as for the processing container 2, 2d of insulators is arranged between top-face 2a and the ball lightning pole 3. Glass and the product made from plastics are sufficient not only as this but all, and if the quality of the material of the processing container 2 has taken the electrode and the insulation, metal, such as stainless steel and aluminum, is sufficient as it.

[0017] The upside ball lightning pole 3 and the lower plate electrode 4 with which a pair counters are arranged in the processing container 2. Although it is an electrode which has the spherical surface and a true ball, ellipse balls, or those semi-spheres are also available for it, since the upside ball lightning pole 3 tends to perform surface treatment with a uniform true ball, it is desirable. Since surface treatment becomes impossible the shape of a pattern when it becomes larger than the lower plate electrode 4, the diameter of the ball lightning pole 3 is made smaller than the lower plate electrode 4. Although the diameter of the ball lightning pole 3 can carry out surface treatment in the shape of a pattern so vividly that it is small, if too small, since it will become easy to generate arc discharge by high-voltage impression, its diameter of 1mm or more is desirable. Moreover, a massive object or a hollow object is also available for the ball lightning pole 3.

[0018] The lower plate electrode 4 is made into the configuration which is in agreement with a desired processing pattern. As a flat-surface configuration of a plate electrode 4, if it is a match, the configuration which has centrum 4a like an alphabetic character like drawing 2 or drawing 3 arbitrarily will be mentioned to a desired processing pattern. Moreover, as shown in drawing 4, you may be arranged so that two or more electrode 4b may form a pattern, and it can be regarded as the electrode connected by connecting each electrode to juxtaposition or a serial, and, thereby, can patternize.

[0019] Moreover, although especially the line breadth of a pattern is not limited, since the excitation kind in the discharge plasma will arrive also at a field without a pattern and the pattern as a plate electrode configuration will no longer be formed if line spacing is too narrow, it is 5mm or more to take 1mm or more desirable still more preferably.

[0020] Although the quality of the material of a ball lightning pole and a plate electrode is used as a metal, the metal which consists of multicomponent like stainless steel or brass in this case, or a pure metal like copper or aluminum is also available for it. Moreover, physical vapor deposition with which a plate electrode 4 carries out coating of the conductive paint to the below-mentioned solid dielectric, such as approach; sputtering, ion plating, and vacuum deposition; a metal thin film may be formed by the dry process methods, such as chemical vapor deposition, such as plasma CVD, and thermal spraying. In addition, when forming an electrode with a thin film, in order to consider as the continuation film, 100A or more is required.

[0021] Although it faces impressing an electrical potential difference to an electrode and you may carry out from which electrode, it is safer to impress from the direction of the small ball lightning pole of an electrode surface product.

[0022] In this invention, the field which counters other electrodes of one [ at least ] electrode is completely covered with the solid dielectric. In the equipment of drawing 1, the solid dielectric 5 is arranged on the plate electrode 4. A solid dielectric 5 needs to be arranged all over the opposed face of the electrode which faces. If the opposed face is exposed, arc discharge will also produce a part at the time of plasma treatment. If the substrate to process is a non-conductive thing, a solid dielectric should just be arranged by the opposed face of one of electrodes, but if a substrate is a conductive thing like a metal, it is necessary to arrange a solid dielectric in both electrodes.

[0023] As a solid dielectric 5, for example, ceramics, such as titanate-acid compounds, such as plastics; silicas, such as polytetrafluoroethylene (PTFE) and polyethylene terephthalate (PET), an alumina, titanium oxide, and barium titanate, is mentioned, and since a dielectric with higher specific inductive capacity can

be processed with low power, the titanium oxide and the titanate compound which are a ferroelectric are more desirable.

[0024] As a solid dielectric 5, the shape of a sheet and a film is also available. However, if dielectric breakdown will happen at the time of electrical-potential-difference impression, and it will become easy to produce arc discharge, if thickness becomes thin, and it becomes thick, since it will be hard coming to discharge, the thickness of 0.05-4mm is desirable.

[0025] A solid dielectric 5 may cover a dielectric with approaches, such as physical vapor deposition, chemical vapor deposition, thermal spraying, and coating, to an electrode.

[0026] In this invention, the plasma treatment section 6 by the discharge plasma is inter-electrode space which counters. Although the distance between a ball lightning pole and a plate electrode is suitably determined as the quantity of gas flow supplied, the magnitude of applied voltage, the quality of the material of a solid dielectric and thickness, and a list with the thickness of a base material etc., if its intact gas increases, it is inefficient-like, when distance becomes small and becomes large, since the homogeneity of the discharge plasma of electrode space will become is easy to be spoiled, 1-20mm is desirable.

[0027] In order to perform plasma treatment using the equipment of drawing 1, a substrate 7 is installed on the plate electrode 4 with which the solid dielectric 5 was arranged, through the reactant gas installation tubing 8, the ball lightning pole 3 of porous structure to inert gas is supplied to the plasma treatment section 6 from the inert gas installation tubing 9, respectively, and reactant gas is adjusted to the pressure near the atmospheric pressure of the mixed gas of reactant gas and inert gas. The pressure near [ as used in the field of this invention ] the atmospheric pressure is specifically 100 - 800Torr, and 700 - 780Torr is desirable in respect of low-cost-izing of equipment and a facility.

[0028] Next, an electrical potential difference is impressed to an electrode, the discharge plasma is generated, the active species by which it was excited in the plasma is contacted on a substrate front face, and surface treatment of a substrate is performed.

[0029] In addition, although the interior is used as the porous electrode (four puncturing 3b of 1mmphi from which the interior of an electrode is made into a cavity, and specifically turns into the outlet section of gas at the surface section is prepared) set to path 3a of gas in drawing 1 in order that the ball lightning pole 3 may supply reactant gas to homogeneity. Thus, when the ball lightning pole 3 serves both as a gas inlet and an electrode and consists of porous structure, it is desirable in order to supply reactant gas to the plasma treatment section 6 at homogeneity and to perform uniform processing. Moreover, although inert gas may be mixed with reactant gas and you may introduce from the ball lightning pole 3 or the inert gas installation tubing 9, in order to process to homogeneity, it is desirable to separate reactant gas and inert gas and to introduce the ball lightning pole 3 to inert gas only for reactant gas from the inert gas installation tubing 9 as mentioned above. Moreover, as shown in drawing 1, since inert gas and reactant gas tend to be mixed by homogeneity, the direction which it considers as the shape of a ring which surrounds the perimeter of the plasma treatment section 6, or spreads in the plasma treatment section 6, and much hole 9a can open in the ring, and supplies inert gas in the processing container 2 from hole 9a is desirable [ the point in the processing container 2 of the inert gas installation tubing 9 ]. This ring has a desirable product made from glass (for example, Pyrex glass).

[0030] Moreover, although reactant gas and inert gas are not illustrated, it is desirable for control of flow to be carried out and to be supplied with a massflow controller, respectively.

[0031] Moreover, superfluous reactant gas and inert gas are discharged from the gas outlet 10 of the processing container 2. Moreover, in case reactant gas and inert gas are introduced in the processing container 2, it is desirable to exhaust the air which remains in the processing container 2 from an exhaust port 11.

[0032] Moreover, to the atmospheric pressure plasma treatment of water-repellent grant, especially heating and cooling of a substrate are unnecessary, and possible enough under a room temperature to it.

[0033] Moreover, even if the processing time is determined in the magnitude of applied voltage, it \*\*\*\*\* in about 5 seconds in the range of said applied voltage and it processes over the time amount beyond it, water-repellent \*\*\*\*\* does not improve but short-time processing is enough as it.

[0034]

[Example] Hereafter, the example of this invention is explained.

The plasma generator shown in example 1 drawing 1 (the ball lightning pole 3 is a globular form with a diameter of 20mm, it is a product made from brass with a thickness of 3mm, and four phi 1mm puncturing 3b is prepared.) A plate electrode 4 is W typeface shown in drawing 2, are a product made from stainless steel with a thickness of 3mm, and each dimension and include angle in drawing 2 A= 100mm, B= 100mm,

C= 25mm, D= 15mm, E= 10mm, Use and inter-electrode distance is set to 5mm. F= 75 degrees and G= 105 degrees -- it is -- a plate electrode 4 top -- as a solid dielectric 5 -- phi150mm -- a titanium oxide sintered compact (specific inductive capacity --) with a thickness of 2mm About 80 is arranged, the film with a thickness of 50 micrometers made from polyethylene terephthalate (the Toray Industries, Inc. make, trade name lumiler T60) is installed by phi150mm as a substrate 7 on a solid dielectric 5, and it is a rotary pump (not shown) to 10Torr(s) about the air in the processing container 2. the following -- being the same -- it exhausted from the exhaust port 11.

[0035] Subsequently, after introducing 4 fluoride [ carbon ] gas of quantity-of-gas-flow 10sccm in the processing container 2 from hole 9a and making helium gas of quantity-of-gas-flow 990sccm into the atmospheric pressure of 762Torr for it through the gas installation tubing 9 more nearly again than the gas installation tubing 8, the square wave with a frequency of 15kHz was impressed with power (5.5kV and 34mA), was left for 15 seconds, and surface treatment of a substrate 7 was carried out. Plasma luminescence was observed with high-voltage impression.

[0036] Next, phi2mm waterdrop was dropped at the front face of the substrate after processing at intervals of 2mm, and the static contact angle was measured using the contact angle measuring device (trade name CA-D) by the consonance interface science company. Consequently, in the field in which the discharge plasma was irradiated, the high contact angle was shown to Haruka and distribution of the point of measurement of 100 contact angles or more had become the configuration of a plate electrode, and the pattern of the same W character mold from the contact angle (67 degrees) of a substrate.

[0037] Plasma treatment was carried out like the example 1 except having considered as polytetrafluoroethylene (specific inductive capacity, about 2.4) with a thickness of 2mm by phi150mm, and having considered as the electrical potential difference of 17kV, and 78mA of currents as power of plasma treatment instead of the solid dielectric 5 in example 2 example 1. Next, the static contact angle was measured for the front face of the substrate after processing like the example 1. Consequently, in the field in which the discharge plasma was irradiated, the high contact angle was shown to Haruka and distribution of the point of measurement of 100 contact angles or more had become the configuration of a plate electrode, and the pattern of the same W character mold from the contact angle (67 degrees) of a substrate.

[0038] The plasma generator shown in example 3 drawing 1 (ball lightning pole 3 is the same as that of an example 1.) It is what carried out vacuum deposition by 0.3-micrometer thickness so that it might become the square form where it has centrum 4a of four squares like the pattern which showed copper to the titanium oxide sintered compact (specific inductive capacity, about 80, grade TP-3) with a thickness of 2mm by the Fuji titanium company by  $5 \times 10^{-5}$ Torr at drawing 3, by phi150mm as a solid dielectric 5 and a plate electrode 4. in addition, each dimension in drawing 3  $R > 3$  -- A= 68mm, B= 30mm, C= 2mm, and D= 3mm -- it is -- using -- inter-electrode distance -- 7mm -- carrying out -- a solid dielectric 5 top -- the film of the product made from polyethylene with a thickness of 50 micrometers in phi150mm as a substrate 7 -- installing -- the air in the processing container 2 -- up to 10Torr(s) -- a rotary pump (not shown) the following -- being the same -- it exhausted from the exhaust port 11.

[0039] Subsequently, after introducing the mixed gas of 4 fluoride [ carbon ] gas of quantity-of-gas-flow 3sccm, and the oxygen gas of 7sccm(s) in the processing container 2 from hole 9a and making helium gas of quantity-of-gas-flow 990sccm into the atmospheric pressure of 757Torr for it through the gas installation tubing 9 more nearly again than the gas installation tubing 8, the square wave with a frequency of 20kHz was impressed with power (7kV and 41mA), was left for 60 seconds, and surface treatment of a substrate 7 was carried out. Plasma luminescence was observed with high-voltage impression.

[0040] Next, the static contact angle of the front face of the substrate after processing was measured like the example 1. Consequently, in the field in which the discharge plasma was irradiated, the low contact angle was shown to Haruka and distribution of the point of measurement of 45 or less contact angles had become the same pattern as the configuration of a plate electrode from the contact angle (88 degrees) of a substrate. Therefore, it turned out that hydrophilization is carried out by the same pattern as the configuration of a plate electrode.

[0041] The plasma generator shown in example 4 drawing 1 (the ball lightning pole 3 is a globular form with a diameter of 10mm, it is a product made from stainless steel with a thickness of 3mm, and four phi1mm puncturing 3b is prepared.) It is what was 0.2-micrometer thickness about copper in  $2 \times 10^{-5}$ Torr, carried out vacuum deposition to a configuration with which with an one-side square [ 30mm square ] electrode 4b was compared at spacing they are [ spacing ] four pieces and 2mm as shown at drawing 4, and, subsequently to juxtaposition, carried out silver soldering of the lead wire to the quartz dielectric (specific inductive capacity, 4.5) with a thickness of 2mm between each isolated electrode 4b [ each ] by phi140mm

as a solid dielectric 5 and a plate electrode 4. in addition, each dimension in drawing 4 -- A= 30mm and B= 2mm -- it is -- using -- inter-electrode distance -- 3mm -- carrying out -- a solid dielectric 5 top -- the film of the product made from polyethylene with a thickness of 50 micrometers in phi140mm as a substrate 7 -- installing -- the air in the processing container 2 -- up to 10Torr(s) -- a rotary pump (not shown) the following -- being the same -- it exhausted from the exhaust port 11.

[0042] Subsequently, after introducing the gas which mixed the nitrogen gas of quantity-of-gas-flow 5sccm, and helium gas of quantity-of-gas-flow 995sccm in the processing container 2 and making it into the atmospheric pressure of 757Torr from hole 9a through the gas installation tubing 9, the square wave with a frequency of 15kHz was impressed with power (5.5kV and 34mA), was left for 60 seconds, and surface treatment of a substrate 7 was carried out. Plasma luminescence was observed with high-voltage impression.

[0043] Next, the static contact angle of the front face of the substrate after processing was measured like the example 1. Consequently, in the field in which the discharge plasma was irradiated, the low contact angle was shown to Haruka and distribution of the point of measurement of 45 or less contact angles had become the same pattern as the configuration of a plate electrode from the contact angle (88 degrees) of a substrate. Therefore, it turned out that hydrophilization is carried out by the same pattern as the configuration of a plate electrode. However, about nine points that a contact angle was about 60 degrees existed.

[0044] In example of comparison 1 example 1, everything but having not arranged a solid dielectric 5 and having set the pressure of plasma treatment to 0.1Torr instead of 762Torr(s) carried out surface treatment to the plate electrode 4 like the example 1. The discharge plasma showed the configuration which spread as compared with the example 1. Next, the static contact angle was measured for the front face of the substrate after processing like the example 1. Consequently, although the field in which the discharge plasma was irradiated showed the high contact angle of 100 degrees or more to Haruka rather than the contact angle (67 degrees) of a substrate, the pattern of the W character mold as the configuration of a plate electrode with the same distribution of the point of measurement of 100 contact angles or more did not become.

[0045]

[Effect of the Invention] The configuration of the surface treatment approach of the substrate of this invention is as above-mentioned, carries out surface treatment of some substrates by the plasma partially, and offers the simple approach for performing plasma surface treatment in the shape of [ desired ] a pattern. Moreover, compared with the surface treatment approaches, such as plastics by the conventional low voltage glow discharge plasma, it does not need equipment and to be furnished for special vacuum formation, but moreover, the special actuation for it is also unnecessary, and it excels in the cost fall effectiveness, and handling is easy. Therefore, it may be used for adhesion, the paint field, etc. of plastics, a metal, a ceramic, etc., and the repercussion effect is large.

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[Translation done.]

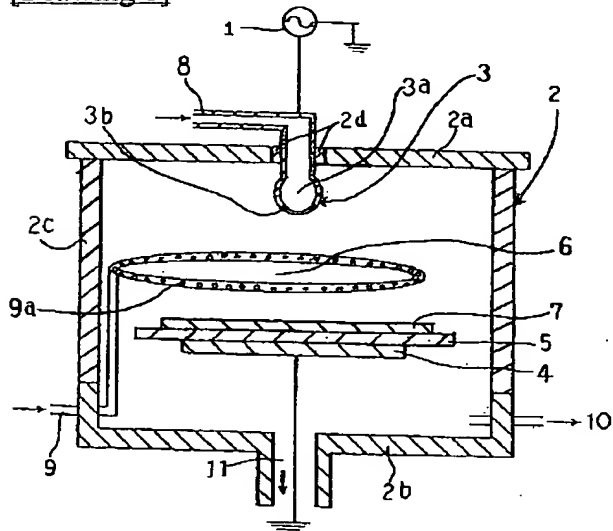
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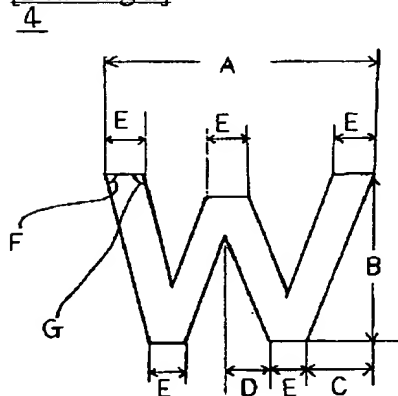
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## DRAWINGS

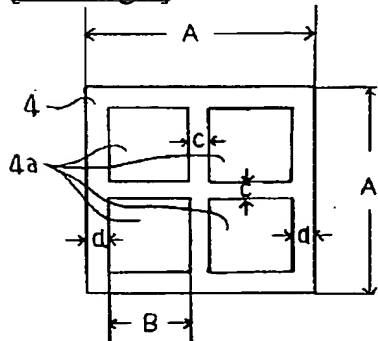
[Drawing 1]



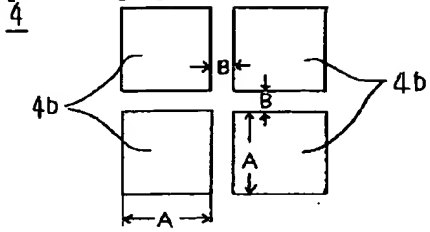
[Drawing 2]



[Drawing 3]



[Drawing 4]



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[Translation done.]

## PATENT ABSTRACTS OF JAPAN

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(71)Applicant : SEKISUI CHEM CO LTD

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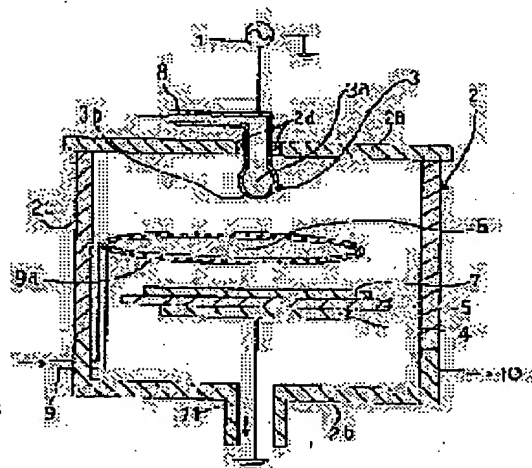
(72)Inventor : YUASA MOTOKAZU  
KAWAI SHIGEMASA

## (54) SURFACE TREATMENT OF SUBSTRATE

## (57)Abstract:

**PURPOSE:** To provide a simple method for executing plasma surface treatment in a desired pattern form by bringing an active species excited in plasma into contact with a substrate surface and subjecting this substrate to the surface treatment.

**CONSTITUTION:** The substrate 7 is installed onto a flat plate electrode 4 disposed with a solid dielectric substance 5. Reactive gases are supplied from a spherical electrode 3 of a porous structure through a reactive gases introducing pipe 8 and an inert gas from an inert gas introducing pipe 9 respectively into a plasma treating section 6 where the gaseous mixture composed of the reactive gases and the inert gas is regulated to the pressure near the atm. pressure. Discharge plasma is generated by impressing voltage to the electrode 3. The active species excited in the plasma is brought into contact with the substrate 7 surface, by which the substrate 7 is subjected to the surface treatment with the patterns similar to the shape of the flat plate electrode 4. As a result, there is no need for special operation and the effect of reducing the cost is excellent. In addition, handling is facilitated.



## LEGAL STATUS

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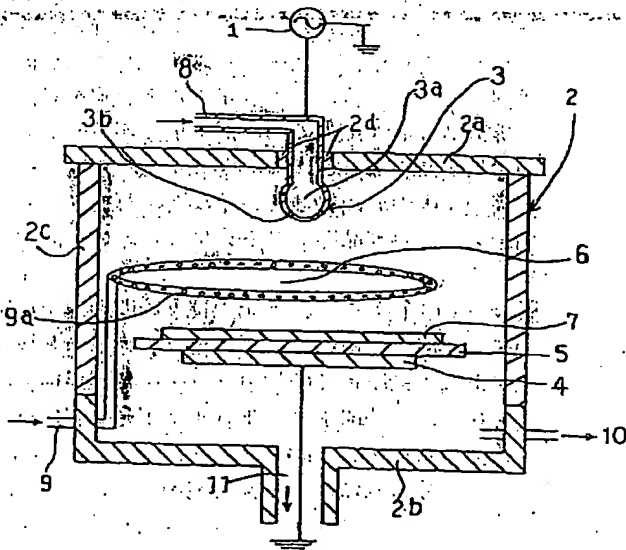
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(54) 【発明の名称】 基板の表面処理方法

(57) 【要約】

【目的】 基板の一部だけを部分的にプラズマによって表面処理して、所望のパターン状にプラズマ表面処理を行うための、簡便な方法を提供する。

【構成】 それぞれ金属製の球電極3と平板電極4が対向して配置され、平板電極4は所望の表面処理パターンに一致する形状とされ、球電極3の直径が平板電極4よりも小さくされ、少なくとも一方の電極の他の電極に対向する面が固体誘電体5によって完全に覆われている電極間に基板7を設置し、反応ガスと不活性ガスとの混合ガスの大気圧近傍の圧力で、電極に電圧を印加し放電プラズマを発生させ、そのプラズマ中の励起された活性種を基板表面に接触させて、平板電極形状と同様のパターンで基板を表面処理することを特徴とする。



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## 【特許請求の範囲】

【請求項1】それぞれ金属製の球電極と平板電極が対向して配置され、平板電極は所望の表面処理パターンに一致する形状とされ、球電極の直径が平板電極よりも小さくされ、少なくとも一方の電極の他の電極に対向する面が固体誘電体によって完全に覆われている電極間に基板を設置し、反応ガスと不活性ガスとの混合ガスの大気圧近傍の圧力で、電極に電圧を印加し放電プラズマを発生させ、そのプラズマ中の励起された活性種を基板表面に接触させて、平板電極形状と同様のパターンで基板を表面処理することを特徴とする基板の表面処理方法。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】本発明は、例えば、プラスチック、紙、金属、ガラス、セラミックス等の基板の表面処理方法に関し、さらに詳しくは、基板の一部だけを部分的にプラズマによって表面処理して、所望のパターン状にプラズマ表面処理を行うための方法に関する。

## 【0002】

【従来の技術】従来より、例えば、プラスチック、紙、金属、ガラス、セラミックス等の基板の表面の濡れ性制御や表面修飾の方法として、 $0.1 \sim 10 \text{ Torr}$ 程度の低圧のグロー放電プラズマによる表面処理方法が広く知られており、産業的にも応用されている。この表面処理方法においては、上記の圧力よりも高い圧力になると、放電が局所的になりアーク放電に移行してしまい、耐熱性の乏しいプラスチックや紙のような基板への利用が困難となるので、通常、あらゆる基板に適用できるように上記の圧力範囲が選ばれている。そのため、真空（もしくは低圧）にする必要上、処理用の容器は高価な真空チャンバーを必要とし、また真空排気装置が必要とされる。さらに、真空中で処理するため大面積の基板に処理しようとする、大容量の真空容器を必要とし、真空排気装置も大出力のものが必要である。そのため、設備費用が高くなるという問題点があった。また、吸水率の高い基板の表面処理を行う場合、真空にするのに長時間を要し、処理品がコスト高になるという問題点もあった。

【0003】そこで、上記の種々の問題点を克服するために、装置、設備の低コスト化と、大面積基板への処理が可能で大気圧下での放電プラズマ処理が提案されてきた。例えば、特開平2-15171号公報には、電極表面に固体誘電体を配設する方法によって、特公平2-48626号公報には、細線型電極を用いる方法によって大気圧下で放電プラズマを行う表面処理方法が提案されている。これらの提案では、ヘリウムを主とする不活性ガスと反応ガスとの混合ガスを、複数の開孔を有する多孔管から基板近傍に供給してプラズマ処理する方法が用いられている。

【0004】これらの従来の低圧や大気圧での放電プラ

ズマ処理技術では、基板の一部だけを部分的に表面処理して、パターン状に表面処理を行う場合には、例えば、特開平1-124847号公報に記載の感光性樹脂などを塗布して不必要な部分をマスクし、プラズマ処理後マスクを除去する方法が提案されている（山岡亜夫、森田浩著、感光性樹脂、共立出版社（1988））。しかし、この方法では、工程が複雑になるという問題点があった。

## 【0005】

【発明が解決しようとする課題】本発明の目的は、基板の一部だけを部分的にプラズマによって表面処理して、所望のパターン状にプラズマ表面処理を行うための、簡便な方法を提供することにある。

## 【0006】

【課題を解決するための手段】本発明の基板の表面処理方法は、それぞれ金属製の球電極と平板電極が対向して配置され、平板電極は所望の表面処理パターンに一致する形状とされ、球電極の直径が平板電極よりも小さくされ、少なくとも一方の電極の他の電極に対向する面が固体誘電体によって完全に覆われている電極間に基板を設置し、反応ガスと不活性ガスとの混合ガスの大気圧近傍の圧力で、電極に電圧を印加し放電プラズマを発生させ、そのプラズマ中の励起された活性種を基板表面に接触させて、平板電極形状と同様のパターンで基板を表面処理することを特徴とする。

【0007】本発明において、基板の表面処理とは、主として、表面官能基層の形成やフリーラジカル層の形成や親水性や撥水性の薄膜を形成することなどによって、基板の表面特性を制御し、基板の濡れ性や接着性を改質することや、基板表面に無機質や有機質の薄膜を形成させて、基板に化学的、機械的、光学的、電気的特性等を付与することを指す。

【0008】本発明で用いられる反応ガスとしては、放電プラズマ中で活性化され基板と接触されて、基板に撥水性を付与したり、親水性を付与したりするガスが挙げられる。例えば、基板に撥水性を付与する場合には、フッ素含有のガスが用いられる。フッ素含有のガスとしては、4フッ化炭素（ $\text{CF}_4$ ）、6フッ化炭素（ $\text{CF}_3\text{CF}_3$ ）、6フッ化プロピレン（ $\text{CF}_3\text{CF}_2\text{CF}_3$ ）等のフッ化炭素ガス、1塩化3フッ化炭素（ $\text{CClF}_3$ ）等のハロゲン化炭素ガス、6フッ化硫黄（ $\text{SF}_6$ ）等のフッ化硫黄化合物、およびこれらの化合物のフッ素の一部が水素に置換された化合物が挙げられる。これらのうち、安全でフッ化水素等の有毒ガスを生成しない、4フッ化炭素や6フッ化炭素などが好ましい。

【0009】また、親水性を付与する場合には、表面にカルボニル基、ヒドロキシル基、アミノ基等の官能基を有する層を形成させるために、炭化水素化合物のガスを使用する。上記炭化水素化合物としては、例えば、メタン、エタン、プロパン、ブタン、ペンタン、ヘキサン等

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のアルカン類；エチレン、プロピレン、ブテン、ペンテン等のアルケン類；ペンタジエン、ブタジエン等のアルカジエン類；アセチレン、メチルアセチレン等のアルキン類；ベンゼン、トルエン、キシレン、インデン、ナフタレン、フェナントレン等の芳香族炭化水素類；シクロプロパン、シクロヘキサン等のシクロアルカン類；シクロペンテン、シクロヘキセン等のシクロアルケン類；メタノール、エタノール等のアルコール類；アセトン、メチルエチルケトン等のケトン類；メタナール、エタナール等のアルデヒド類などが挙げられ、これらは、単独で  
10 使用されてもよいし2種以上併用されてもよい。また、この場合、酸素ガス；酸素と水素の混合ガス；水蒸気；アンモニアガス；窒素ガス等を使用することも可能である。また、これらのガス類にフッ素含有のガスを5.0%以下添加してもよいが、この量を超えて添加すると撥水性を示してしまう。上記反応ガスは、均一性よく表面処理をするためには、大気圧近傍の圧力下でガス状態であることが好ましい。

【0.010】また、基板に化学的、機械的、光学的、電気的特性等を付与するために、 $\text{SiO}_2$ 、 $\text{TiO}_2$ 、 $\text{SnO}_2$ 等の金属酸化物薄膜を形成する場合には、水素化  
20 金属ガス、ハロゲン化金属ガス又は金属アルコール等の金属有機化合物のガスもしくは蒸気が用いられる。

【0.011】本発明で用いられる不活性ガスとしては、 $\text{He}$ 、 $\text{Ne}$ 、 $\text{Ar}$ 、 $\text{Xe}$ 等の希ガスの単体又は混合ガスが用いられるが、準安定励起状態の寿命が長く反応ガスを励起分解するのに有利な $\text{He}$ を用いるのが好ましい。

$\text{He}$ 以外の不活性ガスを使用する場合は、2体積%以内のアセトンやメタノール等の有機物蒸気やメタノール、エタノール等の炭化水素ガスを混合する必要がある。  
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【0.012】基板に撥水性を付与する場合、フッ素含有のガスと不活性ガスとの混合比は、格別限定的ではないが、フッ素含有のガスが10体積%以上になると高電圧を印加しても放電プラズマが発生しないため、10体積%未満が好ましく、フッ素含有のガスの使用量が少なくて撥水性の付与が可能な0.3～5.0体積%が好ましい。

【0.013】本発明に使用される基板は、材質、形状等は特に限定されず、プラスチック、金属、ガラス、セラミック、紙、繊維等が挙げられ、無孔質でも多孔質でも構わない。プラスチックとしては、例えば、ポリエチレンテレフタレートやポリエチレンナフタレート等のポリエステル；ポリエチレン又はポリプロピレン等のポリオレフィン；ポリスチレン；ポリアミド；ポリ塩化ビニル；ポリカーボネート；ポリアクリロニトリル等のフィルムあるいはシートが使用できる。フィルムの場合、延伸されたものでも未延伸のものでも構わない。また、表面洗浄や表面活性化の公知の処理を行ったものでも構わない。

【0.014】以下にプラスチック基板の表面に撥水性を

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付与する場合を例に、図に基づいて本発明を詳細に説明する。図1は、本発明に使用されるプラズマ発生装置の一例を示す模式的な断面図である。本装置は、電源部1、処理容器2、対向して配置された球形の球電極3および平板状の平板電極4から構成されている。

【0.015】電源部1は5～100kHz台の周波数の電圧を印加可能とされており、耐熱性の低い基板の処理には基板への影響の少ない10～30kHzの周波数が好ましい。放電プラズマ形成は電極に電圧を印加することにより行うが、印加電圧が低くなると、プラズマ密度及びセルフバイアスが小さくなるため、処理に時間がかかり非能率的であり、高くなると、アーク放電に移行する挙動を示すので、電界強度5～40kV/cm程度になるように電圧を印加するのが好ましい。

【0.016】処理容器2は、上面2aと底面2bがステンレス製、側面2cがパイレックスガラス製であり、上面2aと球電極3との間に絶縁体2dが配設されている。処理容器2の材質は、これに限らず、全てがガラス製、プラスチック製でも構わないし、電極と絶縁がとれているならばステンレスやアルミニウム等の金属製でも構わない。

【0.017】処理容器2内に一對の対向する上部の球電極3と下部の平板電極4が配設されている。上部の球電極3は、球面を有する電極のことであり、真球でも楕円球でも、またそれらの半球でも構わないが、真球が均一な表面処理を行ない易いので好ましい。球電極3の直径は、下部の平板電極4よりも大きくなるとパターン状に表面処理ができなくなるので、下部の平板電極4よりも小さくされる。球電極3の直径は、小さくほど鮮明にパ  
30 ターン状に表面処理できるが、小さ過ぎると、高電圧印加によってアーク放電が発生し易くなるので直径1mm以上が好ましい。また、球電極3は、塊状体でも中空体でも構わない。

【0.018】下部の平板電極4は、所望の処理パターンに一致する形状とされる。平板電極4の平面形状としては、所望の処理パターンに一致するものであれば、任意であり、例えば、図2のような文字や図3のような中空部4aを有する形状が挙げられる。また、図4に示すように、複数の電極4bがパターンを形成するように配置されていてもよく、それぞれの電極を並列あるいは直列に結線することにより連結された電極とみなすことができ、これによりパターン化できる。

【0.019】また、パターンの線幅は特に限定されないが、線間隔は狭すぎると放電プラズマ中の励起種がパターンがない領域にも到達してしまい、平板電極形状通りのパターンが形成されなくなるので、1mm以上をとるのが好ましく、さらに好ましくは5mm以上である。

【0.020】球電極と平板電極の材質は、金属とされるが、この場合、ステンレスや真鍮のような多成分からなる金属でも、銅やアルミニウムのような純金属でも構わ

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ない。また、平板電極4は、後述の固体誘電体に、導電性塗料を塗工する方法；スパッタリング、イオンプレーティング、真空蒸着等の物理蒸着法；プラズマCVD等の化学蒸着法および溶射等のドライプロセス法で金属薄膜を形成しても構わない。なお、電極を薄膜で形成する場合は、連続膜とするには、100Å以上が必要である。

【0021】電極に電圧を印加するに際しては、どちらの電極から行ってもよいが、電極面積の小さい球電極の方から印加する方が安全である。

【0022】本発明においては、少なくとも一方の電極の他の電極に対向する面が固体誘電体によって完全に覆われている。図1の装置においては、平板電極4の上に固体誘電体5が配設されている。固体誘電体5は、相対する電極の対向面の全面に配設される必要がある。一部でも、対向面が露出しているとプラズマ処理時にアーク放電が生じる。処理する基板が非導電性のものであれば、固体誘電体はどちらか一方の電極の対向面に配設されればよいが、基板が金属等のように導電性のものであれば、両方の電極に固体誘電体を配設する必要がある。

【0023】固体誘電体5としては、例えば、ポリテトラフルオロエチレン（PTFE）やポリエチレンテレフタレート（PET）等のプラスチック；シリカ、アルミナ、酸化チタン、チタン酸バリウム等のチタン酸化合物などのセラミックスが挙げられ、比誘電率の高い誘電体ほど低電力で処理可能であるため、強誘電体である酸化チタンおよびチタン酸化合物がより好ましい。

【0024】固体誘電体5としては、シート状でも、フィルム状でも構わない。しかるに厚みが薄くなると、電圧印加時に絶縁破壊が起こってアーク放電が生じやすくなり、厚くなると、放電じにくくなるので、0.05～4mmの厚みが好ましい。

【0025】固体誘電体5は、電極に誘電体を物理蒸着法、化学蒸着法、溶射および塗工等の方法で被覆してもよい。

【0026】本発明において、放電プラズマによるプラズマ処理部6は、対向する電極間の空間である。球電極と平板電極の間の距離は、供給されるガス流量、印加電圧の大きさ、固体誘電体の材質及び厚み、並びに基材の厚み等によって、適宜決定されるが、距離が小さくなると未使用のガスが多くなり非効率であり、大きくなると、電極空間の放電プラズマの均一性が損なわれ易くなるので、1～20mmが好ましい。

【0027】図1の装置を使用してプラズマ処理を行うには、固体誘電体5が配設された平板電極4の上に基板7を設置し、反応ガスを反応ガス導入管8を経て多孔構造の球電極3から、不活性ガスを不活性ガス導入管9から、それぞれ、プラズマ処理部6に供給し、反応ガスと不活性ガスの混合ガスの大気圧近傍の圧力に調整する。本発明でいう大気圧近傍の圧力とは、具体的には100

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～800Torrのことであり、装置、設備の低コスト化の点で700～780Torrが好ましい。

【0028】次に、電極に電圧を印加して放電プラズマを発生させ、そのプラズマ中の励起された活性種を基板表面に接触させて基板の表面処理を行う。

【0029】なお、図1においては、球電極3は、反応ガスを均一に供給するために、その内部がガスの通路3aとされた、多孔性の電極（具体的には、電極の内部が空洞とされ表面部にガスの出口部となる1mmφの開孔3bが4個設けられている）とされているが、このように球電極3がガス導入口と電極を兼ね、且つ多孔構造からなると、反応ガスをプラズマ処理部6に均一に供給して、均一な処理を行うために好ましい。また、不活性ガスは反応ガスと混合して球電極3または不活性ガス導入管9から導入しても構わないが、均一に処理するには、上述のように、反応ガスと不活性ガスを分離して、反応ガスのみを球電極3から、不活性ガスを不活性ガス導入管9から導入するのが好ましい。また、不活性ガス導入管9の処理容器2内の先端部は、図1に示すように、プラズマ処理部6の周囲を取り巻くか又はプラズマ処理部6内に広がるようなリング状とされ、そのリングに多数の穴9aが開けられ、その穴9aから不活性ガスを処理容器2内に供給する方が、不活性ガスと反応ガスが均一に混合され易いので好ましい。このリングは、ガラス（例えば、パイレックスガラス）製が好ましい。

【0030】また、反応ガスおよび不活性ガスは、図示しないが、それぞれマスフローコントローラーで流量制御されて供給されるのが好ましい。

【0031】また、過剰の反応ガスや不活性ガスは、処理容器2のガス出口10から排出される。また、処理容器2内に反応ガスや不活性ガスを導入する際に、処理容器2内に残存する空気を排気口11から排気するようにするのが好ましい。

【0032】また、撥水性付与の大気圧プラズマ処理には基板の加熱や冷却は、特に必要なく室温下で十分可能である。

【0033】また、処理時間は印加電圧の大きさで決定され、前記印加電圧の範囲では5秒程度で撥水化されておりそれ以上の時間をかけて処理しても撥水化効果は向上せず、短時間の処理で十分である。

【0034】

【実施例】以下、本発明の実施例を説明する。

実施例1

図1に示したプラズマ発生装置（球電極3は直径20mmの球形であり、厚み3mmの真鍮製で、φ1mmの開孔3bが4個設けられている。平板電極4は、図2に示したW字形で、厚み3mmのステンレス製であり、図2におけるそれぞれの寸法および角度は、A=100mm、B=100mm、C=25mm、D=15mm、E=10mm、F=75度、G=105度である）を用

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い、電極間距離を5mmとし、平板電極4の上に固体誘電体5として $\phi 150$ mmで厚み2mmの酸化チタン焼結体(比誘電率、約80)を配設し、固体誘電体5の上に基板7として $\phi 150$ mmで厚み5.0 $\mu$ mのポリエチレンテレフタレート製のフィルム(東レ社製、商品名ルミラーT60)を設置し、処理容器2内の空気を10 Torrまで回転ポンプ(図示せず。以下同じ)で排気口11より排気した。

【0035】次いで、ガス流量10 s.c.c.m.の4フッ化炭素ガスをガス導入管8より、また、ガス流量990 s.c.c.m.のHeガスをガス導入管9を経て穴9aより処理容器2内に導入し、762 Torrの大気圧とした後、周波数15 kHzの矩形波を、5.5 kV、34 mAの電力で印加し15秒間放置して、基板7の表面処理をした。高電圧印加にともなう、プラズマ発光が観察された。

【0036】次に、処理後の基板の表面に $\phi 2$ mmの水 dropletを2mmの間隔で滴下し、協和界面科学社製の接触角測定装置(商品名CA-D)を用いて静的接触角を測定した。その結果、放電プラズマが照射された領域では、基板の接触角(67度)よりも遙に高い接触角を示し、接触角100度以上の測定点の分布は平板電極の形状と同様のW字型のパターンとなっていた。

#### 【0037】実施例2

実施例1における固体誘電体5の代わりに、 $\phi 150$ mmで厚み2mmのポリテトラフルオロエチレン(比誘電率、約2.4)とし、プラズマ処理の電力として電圧17 kV、電流7.8 mAとしたこと以外は、実施例1と同様にしてプラズマ処理をした。次に、処理後の基板の表面を実施例1と同様に静的接触角を測定した。その結果、放電プラズマが照射された領域では、基板の接触角(67度)よりも遙に高い接触角を示し、接触角100度以上の測定点の分布は平板電極の形状と同様のW字型のパターンとなっていた。

#### 【0038】実施例3

図1に示したプラズマ発生装置(球電極3は実施例1と同様。固体誘電体5および平板電極4としては、 $\phi 150$ mmで厚み2mmの富士チタニウム社製の酸化チタン焼結体(比誘電率、約80、グレードTP-3)に、 $5 \times 10^{-5}$  Torrで銅を、図3に示したパターンのように、0.3 $\mu$ m厚みで真空蒸着したもの。なお、図3におけるそれぞれの寸法は、A=68 mm、B=30 mm、C=2 mm、D=3 mmである)を用い、電極間距離を7 mmとし、固体誘電体5の上に基板7として $\phi 150$ mmで厚み5.0 $\mu$ mのポリエチレン製のフィルムを設置し、処理容器2内の空気を10 Torrまで回転ポンプ(図示せず。以下同じ)で排気口11より排気した。

【0039】次いで、ガス流量3 s.c.c.m.の4フッ化炭

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素ガスと7 s.c.c.m.の酸素ガスとの混合ガスをガス導入管8より、また、ガス流量990 s.c.c.m.のHeガスをガス導入管9を経て穴9aより処理容器2内に導入し、757 Torrの大気圧とした後、周波数20 kHzの矩形波を、7 kV、41 mAの電力で印加し60秒間放置して、基板7の表面処理をした。高電圧印加にともなう、プラズマ発光が観察された。

【0040】次に、処理後の基板の表面の静的接触角を実施例1と同様にして測定した。その結果、放電プラズマが照射された領域では、基板の接触角(88度)よりも遙に低い接触角を示し、接触角45度以下の測定点の分布は平板電極の形状と同様のパターンとなっていた。従って、平板電極の形状と同様のパターンで親水化されていることが分かった。

#### 【0041】実施例4

図1に示したプラズマ発生装置(球電極3は直径10 mmの球形であり、厚み3 mmのステンレス製で、 $\phi 1$  mmの開孔3bが4個設けられている。固体誘電体5および平板電極4としては、 $\phi 140$ mmで厚み2 mmの石英誘電体(比誘電率、4.5)に、 $2 \times 10^{-5}$  Torrで銅を、0.2 $\mu$ m厚みで、図4に示したように一辺30 mmの正方形の電極4bが4個、2 mmの間隔で並べられたような形状に真空蒸着し、次いで、それぞれの孤立した各電極4b間にリード線を並列に銀ろう付けしたものの。なお、図4におけるそれぞれの寸法は、A=30 mm、B=2 mmである)を用い、電極間距離を3 mmとし、固体誘電体5の上に基板7として $\phi 140$ mmで厚み5.0 $\mu$ mのポリエチレン製のフィルムを設置し、処理容器2内の空気を10 Torrまで回転ポンプ(図示せず。以下同じ)で排気口11より排気した。

【0042】次いで、ガス流量5 s.c.c.m.の窒素ガスとガス流量995 s.c.c.m.のHeガスを混合したガスをガス導入管9を経て穴9aより処理容器2内に導入し、757 Torrの大気圧とした後、周波数15 kHzの矩形波を、5.5 kV、34 mAの電力で印加し60秒間放置して、基板7の表面処理をした。高電圧印加にともなう、プラズマ発光が観察された。

【0043】次に、処理後の基板の表面の静的接触角を実施例1と同様にして測定した。その結果、放電プラズマが照射された領域では、基板の接触角(88度)よりも遙に低い接触角を示し、接触角45度以下の測定点の分布は平板電極の形状と同様のパターンとなっていた。従って、平板電極の形状と同様のパターンで親水化されていることが分かった。しかし、接触角が60度程度の点が9点程存在した。

#### 【0044】比較例1

実施例1において、平板電極4に固体誘電体5を配設しなかったこと、プラズマ処理の圧力を762 Torrの代わりに、0.1 Torrとしたこと以外は、実施例1と同様にして表面処理した。放電プラズマは、実施例1

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に比較し広がった形状を示した。次に、処理後の基板の表面を実施例1と同様に静的接触角を測定した。その結果、放電プラズマが照射された領域では、基板の接触角(67度)よりも遙に高い100度以上の接触角を示したが、接触角100度以上の測定点の分布は平板電極の形状と同様のW字型のパターンとはならなかった。

【0045】

【発明の効果】本発明の基板の表面処理方法の構成は上述の通りであり、基板の一部だけを部分的にプラズマによって表面処理して、所望のパターン状にプラズマ表面処理を行うための、簡便な方法を提供する。また、従来の低圧グロー放電プラズマによるプラスチック等の表面処理方法にくらべて、特別な真空形成のための装置・設備が必要でなく、しかも、そのための特別な操作も不必要であり、コスト低下効果に優れ、かつ、取扱が容易である。従って、プラスチック、金属、セラミック等の接着や塗装分野等に利用され得、その波及効果は大きい。

【図面の簡単な説明】

【図1】図1は、本発明の表面処理方法に使用されるプラズマ発生装置の一例を示す模式的な断面図である。

【図2】図2は、実施例で使用した平板電極の形状を示す平面図である。

【図3】図3は、実施例で使用した平板電極の形状を示

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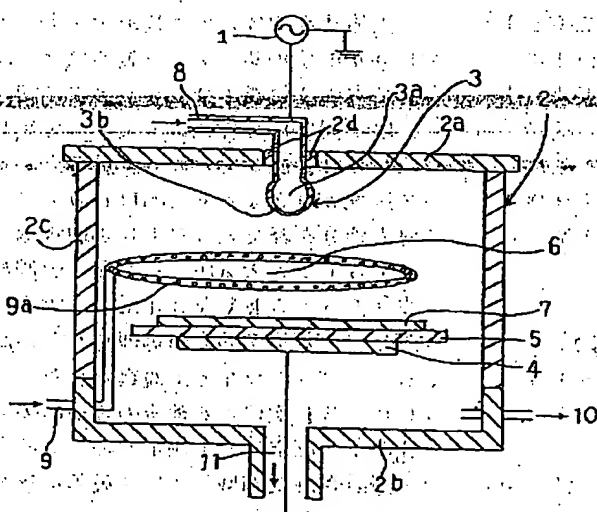
す平面図である。

【図4】図4は、実施例で使用した平板電極の並べ方を示す平面図である。

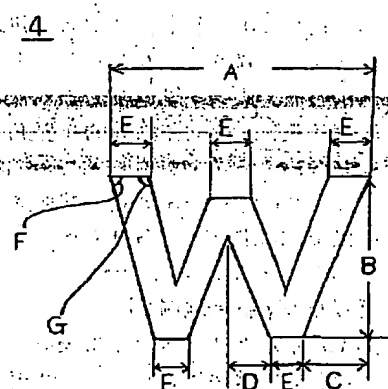
【符号の説明】

- 1 電源部
- 2 処理容器
- 2 a 上面
- 2 b 底面
- 2 c 側面
- 2 d 絶縁体
- 3 球電極
- 3 a ガスの通路
- 3 b 開孔
- 4 平板電極
- 5 固体誘電体
- 6 プラズマ処理部
- 7 基板
- 8 反応ガス導入管
- 9 不活性ガス導入管
- 9 a 穴
- 10 ガス出口
- 11 排気口

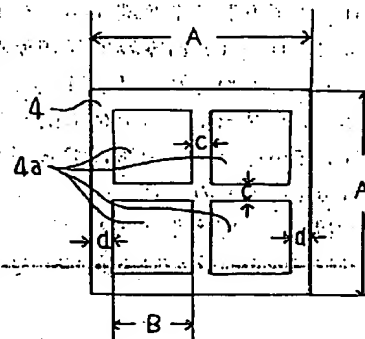
【図1】



【図2】

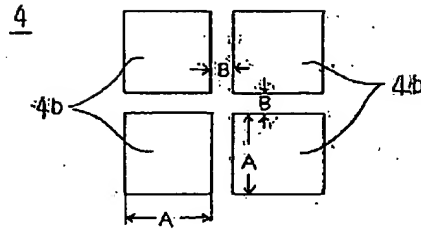


【図3】



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【図 4】



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